Modified NRTL Equation in Predicting Liquid – Liquid Equilibria

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Abstract

The present work deals with fitting literature data of liquid – liquid equilibria and to obtain a new correlation for non-randomness parameter α suitable to use in NRTL activity coefficient model.

New simple correlation is proposed for modifying the original three-parameter NRTL activity coefficient model to make it a true two-parameter model. The performance of the proposed expression is compared with the original three-parameter NRTL activity coefficient model, in correlating LLE data of binary systems, as well as in predicting binary systems from infinite-dilution activity coefficients and ternary systems from binary data.

$$\alpha_{ij} = 0.47 \left(1 + \frac{G_{ij}\,G_{ji}}{2.13} \right)^{-1}$$

To ensure the results had physical significance, the obtained parameters were used to predict the infinite activity coefficients. Properties at infinite dilution are of interest as they usually indicate the maximum non-ideality of the system.

The model was successfully applied to correlate liquid - liquid equilibria, and low temperature activity coefficients. A large database of data was collected for the investigation and it covers a wide range of composition, temperature and pressures. It was found that the proposed form of non-randomness parameter gave the best results.

Keywords: Liquid – Liquid Equilibrium, Activity Coefficient, NRTL.

Introduction

The historical development of thermodynamics has been paved by many people throughout history; through the process of trial and error we have came to accept certain observations as being universal.

The myriad of methods now available to the practicing engineer is evidence that not any one method is overwhelmingly superior; as our collective understanding grows so do the number of models able to describe real mixture behavior.

As a result practitioners may use more than one model to obtain an accurate representation of their system.

It is usually desired to obtain experimental data for the major components in the system under study. This is typically in the form of binary mixture data in the current industrial practice. The binary interaction parameters are introduced. Most industrial systems are composed of more than ten components which made the selected equation calculation not accurate enough compared with experimental data result obtained selected parameter.

Models for the description of real mixture behavior are of fundamental importance for the synthesis, simulation, design, and operation of many separation processes used in industry (e.g. distillation and extraction). Since often 60-80% of the total costs arise in the separation step, a reliable knowledge of the phase equilibrium behavior of the system to be separated is of special importance to industrial practitioners [1].

Many equations have been proposed for the relation between activity coefficients and mole fractions and new ones appear every year. There are two general assumptions in the application of the local composition models. The first is that binary phase equilibrium data is sufficient to obtain the model parameters. The second is that the model parameters are independent of temperature since the models are purported to have built in temperature dependence. These two principles are also applicable to equations of state [2].Models like Wilson, NRTL, and UNIQUAC have long been used with great success for the description of the real behavior of multicomponent mixtures, but they are restricted due to the limited availability of binary interaction parameters [3].

The NRTL equation is suitable for the description of complex phase behavior as expressed by the Gibbs free energy equation of mixing for binary liquid systems with limited miscibility. The determination of the parameters from the miscibility data are very time consuming and gave rise to different solution types depending upon the initial guess, when a search method is used. One of the major benefits of the NRTL model is the increased flexibility in representing the G^E curve over the entire composition range.

The NRTL equation is applicable to partially miscible systems as well as completely miscible mixtures [4].

Further work was even done in an attempt to reduce the NRTL expression to only one parameter by introducing predictions based on pure component properties and molecular structures [5-7], or to reduce the original three-parameter NRTL activity coefficient models to make a two parameter model [8]. However, simplification such led to a loss in accuracy, as compared to the original form of the NRTL equation.

The NRTL model was selected for the current study because of its wide application range and simple implementation. The initial objective of this work is to collect the relevant data available in the public domain for relevant liquid – liquid equilibria, which are commonly used in industry. Secondly, to update the NRTL model used to estimate liquid – liquid equilibria of these systems required in the design of extraction processes. Thirdly, to create an algorithm that can be used to determine the binary interaction parameters of this model from the collected data. Finally, to test the capability of the proposed model to correlate and/or predict the required properties over the composition, temperature and pressure ranges found in industrial separation plants.

The Nrtl Equation

Interpolation and extrapolation of thermodynamic data of liquid mixture are common necessities in chemical engineering. The model of ideal solution is useful for providing a first approximation and a convenient base for the calculation of real properties. But deviations from ideality are frequently significant. These deviations are expressed by excess functions, which depend on the concentration of the components, and the temperature. The most important of these is the excess Gibbs free energy, because the canonical variables for Gibbs energy are temperature and pressure. Since these variables can by directly measured and controlled, the Gibbs free energy is a thermodynamic property of great potential [9-11]. Thus, when G/RT=G (T, P) are given, all other thermodynamic properties can by evaluated by simple mathematical calculations.

Activity coefficient γ_i have traditionally been calculated from correlating equations for G^E/RT by applying the following equation:

$$\ln \gamma_i = \left[\frac{\partial \left(nG^E / RT \right)}{\partial n_i} \right] \quad \ldots\ldots (1)$$

The NRTL (non random two liquid) was originally developed and presented by Renon and

Prausnitz [11], as an empirical model which could improve over the Wilson equation for the simultaneous representation of liquid-liquid equilibria, heat of mixing, and activity coefficient in binary and multicomponent mixtures.

This equation is based on Scott's two-liquid model theory, taking into account nonrandomness in liquid mixture. The nonrandomness parameter α made the NRTL equation applicable to a large variety of binary mixtures and gave a good prediction of ternary liquid-liquid equilibria based on binary data only. $\alpha_{12}(\alpha_{12} = \alpha_{21})$ is a constant characteristic of the norandomness of the mixture.

The NRTL model was an empirical equation based on the local composition representation of the excess Gibbs free energy, G^E, of liquid mixtures. The NRTL expression for the Gibbs free energy is [9-11]:

$$G^E = x_1 x_2 \left[\tau_{21} \frac{G_{21}}{x_1 + x_2 G_{21}} + \tau_{12} \frac{G_{12}}{x_2 + x_1 G_{12}} \right] \quad \ldots\ldots (2)$$

The activity coefficient for the NRTL equation of component 1 and 2 in a binary mixture are:

$$\ln \gamma_1 = x_2^2 \left[\tau_{21} \left(\frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \tau_{12} \frac{G_{12}}{\left(x_2 + x_1 G_{12} \right)^2} \right] \quad \ldots (3)$$

$$\ln \gamma_2 = x_1^2 \left[\tau_{12} \left(\frac{G_{12}}{x_2 + x_1 G_{12}} \right)^2 + \tau_{21} \frac{G_{21}}{\left(x_1 + x_2 G_{21} \right)^2} \right] \quad \ldots (4)$$

where,

$$\tau_{12} = (g_{12}-g_{22})/RT \qquad \ldots\ldots(5)$$

$$\tau_{21} = (g_{21}-g_{11})/RT \qquad \ldots.(6)$$

and

$$G_{12} = \exp(-\alpha_{12}\tau_{12}) \qquad \ldots.(7)$$

$$G_{21} = \exp(-\alpha_{21}\tau_{21}) \qquad \ldots.(8)$$

g_{ij} and g_{ji} are the energies of interactions between the ii or ij component pairs and α_{12} is the non-randomness parameter.

For multiplication systems, the excess Gibbs energy is calculated as follows:

$$\frac{G^E}{RT} = \sum_{i=1}^{N} x_i \left(\frac{\sum_{j=1}^{N} \tau_{ji} G_{ji} x_j}{\sum_{k=1}^{N} G_{ki} x_k} \right) \quad \ldots (9)$$

where,

N is the number of components in the system

$$\tau_{ji} = \frac{g_{ji} - g_{ii}}{RT} \qquad \text{....(10)}$$

$$G_{ji} = \exp\left(-\alpha_{ji}\tau_{ji}\right) \qquad \text{....(11)}$$

The activity coefficient is obtained by equation 12:

$$\ln\gamma_i = \frac{\sum_{j=1}^{N}\tau_{ji}G_{ji}x_j}{\sum_{k=1}^{N}G_{ki}x_k} + \sum_{j=1}^{N}\frac{x_jG_{ij}}{\sum_{l=1}^{N}G_{lj}x_l}\left(\tau_{ij} - \frac{\sum_{r=1}^{N}\tau_{rj}G_{rj}x_r}{\sum_{k=1}^{N}G_{kj}x_k}\right) \quad \text{... (12)}$$

subscript *l* identify species, *j*, *i*, and *k* are dummy indices.

Using model the solubility data to the Non-random Two-Liquid (NRTL) activity coefficient equation to the solute-solvent solubility data to obtain the model binary interaction parameters. Also, using the binary interaction parameters to predict solubility of the model compounds in ternary mixtures (i.e., solute-binary solvent mixtures); and as needed, propose correction to the interaction parameters.

For moderately nonideal systems, the NRTL equation offers no advantages over the simpler van Laar and three-suffix Margules equations. However, for strongly nonideal mixtures, and especially for partially immiscible systems, the NRTL equation often provides a good representation of experimental data if care is exercised in data reduction to obtain the adjustable parameters.

It is superior to the Wilson equation in that it can represent liquid-liquid equilibrium (LLE). Also, it is simpler in form than the UNIQUAC [12] equation but has the main disadvantage of involving three adjustable parameters (G_{ij}, G_{ji}, and $\alpha_{ij} = \alpha_{ji}$) for each pair of components. From both practical and theoretical standpoints, it is desirable to minimize the number of parameters needed to describe as wide a variety of systems as possible. The NRTL equation contains three parameters, but reduction of experimental data for a large number of binary systems indicates that α_{12} varies from about 0.20 to 0.47; yet, when experimental data are scarce, the value of α_{12} can often be set arbitrarily; a typical choice is $\alpha_{12} = 0.3$ [11]. In order to reduce the number of adjustable parameters from three to two in the NRTL equation and to overcome the forecited disadvantage, Renon and Prausnitz [10] recommend $\alpha_{ij} = 0.20$ for partially miscible systems, and all data in the DECHMA LLE collection are correlated with this value for α_{ij}.

For completely miscible systems, Renon and Prausnitz [11], from the reduction of experimental data for a large number of binary systems, found that the third parameter, α_{ij}, varies from 0.20 to 0.47, depending on the chemical nature of the constituents. Consequently, they consider α_{ij} to be an empirical constant, independent of temperature, for which an adequate value can be specified a priori according to empirical rules based on the chemical nature of the mixture's components. However, in a later paper, Renon et al. [9] represented α_{ij} as a linear function of temperature for several mixtures. When α_{ij} is assigned, the NRTL equation has two adjustable parameters, G_{ij} and G_{ji}.

The rules proposed by Renon and Prausnitz [11], which are occasionally ambiguous, classify binary systems into seven main groups (according to polarity and association of the components in the mixture), assigning discrete values (0.2, 0.30, 0.40, and 0.47) for the α_{ij} parameter in these groups. Although α_{ij} has almost no influence for low values of the maximum of the excess Gibbs energy of a binary mixture, it is very useful for strongly nonideal binaries such as polar – nonpolar (alcohol-hydrocarbon) systems. This fact suggests a close relationship between nonideality of the mixture and the value of the α_{ij} parameter and, consequently, the likely existence of an expression for α_{ij} in terms of G_{ij} and G_{ji}. In such a way, for a given system, α_{ij} should change with temperature in a continuous way, decreasing at the same time as temperature increases, i.e. $\alpha_{ij} \propto 1/T$.

The Nonrandomness Parameter α_{ij}

One of the main benefits of the NRTL equation is its ability to represent mixtures exhibiting partial miscibility. Unlike the empirically modified Wilson equation [12-14] the NRTL equation is able to represent multicomponent mixtures (i.e. not just binary mixtures) if given an appropriate nonrandomness factor.

The parameter α is a measure of the non-randomness of the mixture; when α is zero, the mixture is said to be completely random. The NRTL equation provides good representation of the binary vapor-liquid equilibrium and it readily can be generalized for multicomponent mixtures, with only the binary parameters. This equation is superior to the Wilson's equation in the sense that it can represent the liquid-liquid equilibrium (LLE). In addition, it is simpler in form than the UNIQUAC equation. The main disadvantage with the NRTL equation is that it has three adjustable parameters for each pair of components. From both practical and theoretical standpoints, it is desirable to minimize the number of parameters

needed to describe as wide variety of systems as possible.

In the original derivation of the NRTL equation, relationships were drawn between the nonrandomness factor α and Guggenheim's quasichemical approximation it was shown that α was related to the inverse of the coordination number 1/z that appeared in Guggenheim's expression (which can be conceptually considered as 2/z). Renon made an effort to explicitly mention that the nonrandomness parameter was entirely empirical; however it appears that he was clearly guided by the idea that the two quantities were related [10].

Since the coordination number is typically found to be within the range of 6-12 [10, 12, 15], the α parameter was expected to be on the order 0.1 − 0.3 (later revised to 0.2 − 0.47 based on experimental fittings). Even went so as far as to suggest values based on the chemical nature of the mixtures being considered [11] clearly influenced by the idea that α was a property of the mixture, but subsequent studies in the field have eliminated any physical significance originally attributed to the parameter [16-18].

Renon tried to address this issue by attempting to predict the nonrandomness based on the types of mixtures being evaluated [5, 9, 11], however as mentioned, subsequent studies have eliminated any physical significance originally attributed to the parameter (e.g. Tassios [18], even showed that α= −1 works in many cases). In practice the nonrandomness factor α is unceremoniously set to 0.3 (typically results in stable predictions with the NRTL equation), and is typically only treated as an adjustable parameter when warranted (i.e. to fit LLE, or in order to stabilize the prediction) it is entirely considered an empirical factor.

Walas [3] and Demirel and Paksoy [19] suggest that the non-randomness parameter should be forced to vary between 0.1–0.9. In fitting the parameter matrix for the standard groups, it seems prudent to fix the nonrandomness parameter; given that typical values of α vary from 0.2 − 0.47, a fixed value of 0.3 will be used. If the use of a fixed value α=0.3 leads to erroneous results, the parameter will need to be included in the regression of the standard groups. This should support the regression of group parameters that will be generally applicable, a requirement dictated by industrial use of such methods.

Results and Discussion

Proposed Expression For Nonrandomness Parameter α_{ij}

The aim of this work is to find an adequate expression for α_{ij} in terms of G_{ij} and G_{ji} in order to reduce the NRTL equation to a true two-parameter model for systems that are completely miscible in the liquid phase.

Considering the inherent requirements of the α_{ij} parameter and the observed variation of this one with G_{ij} and G_{ji}. we have developed several empirical expressions which lead to values of α_{ij}, in terms of G_{ij} and G_{ji}, ranging from 0 to 0.47. The selected expressions were tested by correlation of experimental LLE data, and it was found that the following simple equation exhibits very good behavior:

$$\alpha_{ij} = 0.47\left(1 + \frac{G_{ij}G_{ji}}{2.13}\right)^{-1} \qquad \ldots (13)$$

Substitution of α_{ij} from eq 13 into 11 and substitution eq 10 and eq 11 into eq 12 gives the equation referred to here as the proposed expression form of the NRTL equation. In order to verify the performance of the proposed expression form, an extensive study was carried out by comparing its behavior in LLE data correlations and predictions with the other two forms of the NRTL equation: (1) three adjustable parameters and (2) α_{ij} parameter set according to Renon's rules [11].

In the first place, for this study, 222 reliable VLE data sets on completely miscible binary systems, at low or moderate pressures, were fitted with the three forecited equations. The systems components include hydrocarbons (paraffinic, naphthenic, and aromatic), ethers, esters, ketones, alcohols, phenol, *m*-cresol, water, and halogen-, nitrogen-, and sulfur-containing compounds. A fitting procedure, based on an algorithm developed by Powell [20], was established to minimize the following equation for the standard deviation, which has been used as the objective function.

$$std\ dev = \left[\frac{\sum_{i=1}^{N}\left[\left[\frac{\gamma_{1,exp}-\gamma_{1,cal}}{\gamma_{1,exp}}\right]^2 + \left[\frac{\gamma_{2,exp}-\gamma_{2,cal}}{\gamma_{2,exp}}\right]^2\right]}{2N-1}\right]^{1/2} \quad \ldots(14)$$

In this fitting procedure, a correction for vapor-phase nonideality was incorporated, and the activity coefficients were obtained from both isothermal and isobaric x, y, T, P data for completely miscible binary systems. The vapor-phase fugacity coefficients were calculated with the Peng and Robinson [21] equation of state and the method of Hayden and O'Connell [22] for computing the second coefficient of the Virial

equation. Similar results were obtained from both equations of state, with the exception of the systems n-pentane + acetone at 149.5, 124.6, and 99.6 °C. For these systems, the values obtained by the method of Hayden and O'Connell were used.

The results are summarized in Table 1, where the correlated binary systems have been classified into five groups according to the average infinite dilution activity coefficients:

$$\gamma_{av}^{\infty} = \left(\gamma_1^{\infty} + \gamma_2^{\infty}\right)\bigg/ 2 \qquad ....(15)$$

The results lead to the following conclusions:
(1) All forms of the NRTL equation perform well, and as one might expect, the best results are obtained from the three-parameter form since this equation uses three adjustable parameters to minimize the objective function.

Table (1): Standard Deviations in Fitting Liquid-Phase Activity Coefficients of Binary Systems

γ_{av}^{∞}	no. of data sets	no. of data points	std dev		
			3- parameter	Renon's rules	Proposed expression
<0.5	14	156	0.054	0.065	0.055
0.5-1.5	62	1095	0.028	0.028	0.028
1.5-5.0	82	1442	0.032	0.034	0.033
5.0-15	47	728	0.031	0.039	0.034
>15	17	303	0.040	0.062	0.042
total	222	3724			
av. of all data sets			0.033	0.037	0.034

(2) For systems with relatively high positive deviations and both positive and negative moderate deviations from ideality ($0.5 < \gamma_{av}^{\infty} < 15$), the Renon rules and the proposed expression forms of the NRTL equation perform well and the proposed expression form shows somewhat better performance than the Renon rules form.
(3) For systems showing both very strong positive ($\gamma_{av}^{\infty} > 15$) and very strong negative ($\gamma_{av}^{\infty} < 0.5$) deviations from ideality, the proposed expression form shows better performance than the Renon rules form.

Estimation of Parameters

A new strategy was explored to estimate the parameter, allowing the experimental solubility data to be fitted to the Non Random Two Liquid (NRTL) activity coefficient model to obtain model energetic interaction parameters. The interaction parameters were successfully used to estimate solubility of the model compounds in mixed solvents over a temperature range.

The suitability of this modification is evaluated by following procedure in order to correlate or to predict the LLE of several binary systems taken from the literature ranged according to their non-ideality degree.

The estimation of the parameters in the NRTL equation was performed by minimizing the objective function (eq. 14).

The objective function was minimized with a hybrid algorithm consisting of the simulated annealing optimization algorithm [23] and either the Simplex [24] Levenberg-Marquardt algorithm [25–26] or Powell's dog-leg method [20]. The simulated annealing method, with enough time should ultimately find the global optimal solution; however due to practical CPU time limitations, a rough (essentially the global minimum) global minimum will most likely be obtained from the algorithm.

In order to optimize the computational effort, the parameters, determined at the rough global optimum can be further refined to obtain the global optimum with the use of standard non-linear optimization technique. This technique, however, will work sufficiently well only if the simulated annealing algorithm has determined a good starting point, i.e. sufficiently close to the global optimum (as required by all non-stochastic optimization algorithms, [27]). This hybrid approach has also been used and recommended by

 [28–29] several authors. The 'optimal' parameters determined from the simulated annealing algorithm were used as the starting point in the local optimization algorithm. Throughout the parameter optimization, the values that dictated the performance of the simulated annealing algorithm (number of iterations, cooling schedule, etc.) were those recommended by Goffee [23].

Temperature Influence on α_{Ij}

An advantage of assuming the additional temperature dependence on α parameter was the improved ability of the model to correlate and predict the non-ideal mixtures.

Results from the correlation of binary systems indicated that the NRTL model performed better with the inclusion of the non-linear temperature dependence in the interaction parameters.

It is considered to be an important advantage in the design of isobaric distillation equipment where the temperature varies from plate to plate [30].

To illustrate the influence of temperature on α_{ij}, such as was suggested in the introduction of this work, in Table 2 the results of the fittings of six sets of experimental isothermal VLE data, corresponding to the n-pentane + acetone system at temperatures ranging from -35 °C to 149.5 °C, are presented [31].

Table (2): Fit of Experimental VLE Data for the n-Pentane (1) + Acetone (2) System from -35 to 149.5 °C.

T, ºC	γ^{∞}_{av}	Renon's rules		Proposed expression	
		α_{12}	Std dev	α_{12}	Std dev
-35.0	16.4	0.20	0.046	0.468	0.012
-15.0	10.2	0.20	0.036	0.447	0.017
25.0	6.7	0.20	0.031	0.423	0.015
99.6	3.7	0.20	0.029	0.387	0.025
124.6	2.4	0.20	0.021	0.379	0.020
149.5	2.2	0.20	0.016	0.376	0.014
av			0.030		0.017

As shown in Table 2, α_{ij} has almost no influence on the standard deviation in the case of high temperatures, from 99.6 °C to 149.5 °C, and both the Renon rules and the proposed expression forms of the NRTL equation lead to similar results. However, at low temperatures, from -35 °C to 25 °C, the influence of α_{ij} is very important, and the standard deviation for the Renon rules form (with respect to the proposed expression form) greatly increases as the temperature reduces. These results suggest that the α_{ij} parameter should be set according not only to the chemical nature of mixture components but also to the temperature. Therefore, assuming that a linear reciprocal absolute temperature dependence for the logarithm of α_{ij} exists, the values of α_{ij} for proposed expression form of the NRTL equation shown in Table 2 were correlated with temperature to obtain the following expression:

$$\ln \alpha_{ij} = -1.2546 + 119.113/T \qquad \text{....(16)}$$

Which provides a very accurate representation of the nonrandomness parameter in terms of the absolute temperature, with an overall average deviation in α_{ij} of only 0.098 %?

Infinite - Dilution Activity Coefficients

Activity coefficient data is necessary for the understanding and design of many unit operations in chemical engineering (crystallization, distillation, liquid-liquid extraction etc.). Usually (but not always) the maximum value of the activity coefficient occurs at the infinite dilution value, which is the limit of the activity coefficient as the concentration of the solute tends towards zero. The infinite dilution activity coefficient is therefore a convenient way to gauge the suitability of a solvent for, as an example, liquid-liquid extraction.

Infinite-dilution activity coefficients play an important role in the analysis of separation processes, and the many advantages of γ^{∞} in characterizing miscible solution behavior are well documented [18]. On the other hand, in recent years a number of new techniques, primarily chromatographic, have been developed for the relatively easy and rapid determination of activity coefficients in the limit of infinite dilution, and

considerable amount of information on limiting activity coefficients is available in the literature [32-33].

The proposed expression form of the NRTL equation is a true two-parameter model, and consequently, the parameters can be calculated from a single experimental data or from a pair of infinite-dilution activity coefficients.

$$\ln \gamma_1^{\infty} = \tau_{21} + \tau_{12} \exp\left(-\alpha\,\tau_{12}\right) \quad \dots(17)$$

$$\ln \gamma_2^{\infty} = \tau_{12} + \tau_{21} \exp\left(-\alpha\,\tau_{21}\right) \quad \dots(18)$$

To ensure the results had physical significance, the obtained parameters were used to predict the infinite activity coefficients. Properties at infinite dilution are of interest as they usually indicate the maximum non-ideality of the system. Therefore, a further test of the proposed expression form was carried out, studying its ability to predict binary LLE from infinite-dilution activity coefficients.

In Table 3, the average absolute error in the vapor mole fraction, calculated using parameters obtained from infinite-dilution activity coefficients, is shown for the Renon's rules and proposed expression forms of the NRTL equation. The $\square_{12}$ parameter set according to Renon's rules for each system is also shown in Table 3. The experimental values of γ_1^{∞} and γ_2^{∞} were obtained by graphic extrapolation to infinite dilution in both dilute regions for each binary pair [34-41].

As shown in Table 3, both forms of the NRTL equation exhibit generally a very good performance and the proposed expression form predicts substantially better than the Renon rules form.

Prediction of Ternary Vapor-Liquid Equilibrium from Binary Data

A study covering 13 ternary miscible systems [42-46] was carried out in order to compare the performance of the three-parameter, Renon's rules, and proposed expression forms of the NRTL equation in predicting multicomponent VLE from binary data. Equation 12 was employed for each form of the NRTL equation, with binary parameters obtained from fitting the binary system and the corresponding activity coefficients and vapor mole fractions were calculated for each ternary system.

The results are presented in Table 4 and indicate that good prediction of ternary VLE can be achieved with all three forms of the NRTL equation. In opposition to what would be expected, both the proposed expression and Renon's rules forms give slightly better results than the original three-parameter NRTL equation. This conclusion agrees with that

previously obtained by Tassios [18], who studied the accuracy of the three-parameter and Renon rules forms of the NRTL equation in predicting the activity coefficients for ternary systems from binary data only. It is interesting to remark that the proposed expression form provides very good prediction of ternary VLE data from binary, at least as good as the NRTL equation with the value of α_{ij} set according to the rules of Renon and Prausnitz [11].

Conclusions

The no randomness parameter α is largely an empirical parameter and may not follow the rules set out by Renon.

Tassios [18] states that the NRTL equation should be considered an empirical model and the best results are obtained when the non-randomness is obtained from regression of the available experimental data. This was also suggested by van Bochove [47], who pointed out that values from 0.01 to 100 can be found from correlations of experimental data.

An optimization algorithm, based on the simulated annealing algorithm, has been developed to optimize the binary interaction parameters in the NRTL model from activity coefficient, LLE data. The model was quite successful in correlating the activity coefficient, LLE data of the systems investigated. The difference in the goodness of fit between the systems can be explained by the quality of data found for each system.

In this work, we have proposed the simple expression in order to reduce the number of adjustable parameters from three to two in the original NRTL equation. The resulting equation, referred to in this paper as the proposed expression form of the NRTL equation, is a true two-parameter model which eliminates the ambiguity encountered sometimes in choosing the proper value of the nonrandomness parameter $\square_{ij}$ according to the rules recommended by Renon and Prausnitz for completely miscible systems.

The performance of both the proposed expression and Renon's rules forms of the NRTL equation is compared in correlating LLE data of binary systems and in predicting binary systems from infinite-dilution activity coefficients and ternary systems from binary data only.

The proposed expression form of the NRTL equation exhibits a very good behavior for both correlation and prediction of LLE data of completely miscible systems. It appears to give better results than the Renon's rules form for correlation of LLE data of binary systems and prediction of ternary systems from binary data only, and it gives better results than the Renon's rules form in predicting binary systems from infinite-dilution activity coefficients.

Table (3): Prediction of Experimental Data from Two Infinite-Dilution Activity Coefficients

no.	system 1-2	T, ºC	exp. γ_1^∞	exp. γ_2^∞	α_{12}	av. abs error in vapor mole fraction Renon's rules	av. abs error in vapor mole fraction Proposed expression
1	water-hydrazine	58-75	0.17	0.03	0.30	0.008	0.006
2	quinoline-m-cresol	180.3	0.10	0.18	0.30	0.012	0.010
3	quinoline-m-cresol	160.4	0.15	0.19	0.30	0.007	0.006
4	quinoline-m-cresol	200.3	0.12	0.30	0.30	0.010	0.008
5	diethyl ether-halothane	30.0	0.23	0.21	0.30	0.005	0.004
6	diethyl ether-halothane	33-51	0.31	0.26	0.30	0.002	0.002
7	benzothiazole-m-cresol	160.3	0.36	0.43	0.30	0.010	0.008
8	chloroform-ethyl acetate	63-78	0.54	0.36	0.30	0.003	0.002
9	acetone-chloroform	45.0	0.44	0.47	0.30	0.008	0.006
10	acetone-acetonitrile	45.0	1.05	1.04	0.30	0.008	0.006
11	n-octane-2-methylpentane	40.0	1.18	1.04	0.30	0.006	0.005
12	methylcyclopentane-benzene	71-80	1.47	1.34	0.30	0.002	0.002
13	acetone-benzene	45.0	1.65	1.52	0.30	0.005	0.004
14	acetone-carbon tetrachloride	45.0	3.00	2.15	0.30	0.009	0.007
15	n-pentane-acetone	149.5	2.82	2.50	0.20	0.030	0.023
16	benzene-acetonitrile	70.0	2.70	2.65	0.30	0.007	0.006
17	benzene-acetonitrile	73-82	2.55	3.15	0.30	0.008	0.006
18	n-pentane-acetone	124.6	3.15	2.98	0.20	0.027	0.021
19	n-pentane-acetone	99.6	3.57	3.64	0.20	0.027	0.020
20	diethylamine-acetonitrile	24.8	3.65	4.10	0.30	0.008	0.006
21	n-pentane-acetone	25.0	6.56	8.04	0.20	0.028	0.014
22	acetone-cyclohexane	25.0	8.50	6.50	0.20	0.016	0.004
23	ethanol-benzene	45.0	10.60	4.45	0.47	0.005	0.005
24	butanol-carbon disulfide	30.0	13.00	2.60	0.47	0.003	0.003
25	acetonitrile-triethylamine	70-87	9.00	9.00	0.47	0.010	0.009
26	nitromethane-carbon tetrachloride	45.0	10.60	7.45	0.47	0.007	0.004
27	carbon tetrachloride-acetonitrile	65-80	5.00	15.00	0.47	0.020	0.016
28	n-pentane-acetone	-15.0	11.48	12.36	0.20	0.038	0.010
29	ethanol-methylcyclopentane	60-77	20.00	5.75	0.47	0.012	0.009
30	ethanol-n-hexane	58-68	18.10	9.05	0.47	0.009	0.008
31	n-pentane-acetone	-35.0	14.13	15.21	0.20	0.035	0.002
32	ethanol-n-heptane	30.0	20.00	14.00	0.47	0.012	0.010
33	ethanol-n-heptane	30.1	23.00	12.50	0.47	0.005	0.004
34	ethanol-isooctane	50 0	27.50	10.80	0.47	0.014	0.012
35	ethanol-carbon disulfide	30.0	53.00	6.50	0.47	0.010	0.008
	av					**0.012**	**0.008**

Table (4) Prediction of Ternary Systems from Binary VLE Data

no.	component 1	component 2	component 3	P or T	no. of data points	av. abs error in vapor mole fraction 3-parameter	av. abs error in vapor mole fraction Renon's rules	av. abs error in vapor mole fraction Proposed expression
1	cyclohexane	cyclohexene	1,2-dichloroethane	760 mmHg	42	0.013	0.013	0.010
2	n-hexane	benzene	tert-butyl alcohol	760 mmHg	116	0.010	0.010	0.008
3	n-hexane	benzene	I-butanol	55 ºC	25	0.012	0.011	0.009
4	2-butanone	benzene	acetonitrile	55 ºC	25	0.004	0.004	0.003
5	2,4-dimethylpentane	cyclohexane	tert-butyl alcohol	760 mmHg	37	0.012	0.011	0.009
6	benzene	perfluorobenzene	melhylcyclohexane	760 mmHg	142	0.009	0.006	0.004
7	ethyl acetate	cyclohexane	tetrmhydrofuran	40 ºC	34	0.005	0.006	0.005
8	acetone	methanol	water	760 mmHg	55	0.028	0.020	0.015
9	chloroform	benzene	2-propanol	50 ºC	5	0.009	0.009	0.006
10	acetone	chloroform	methanol	760 mmHg	5	0.008	0.007	0.004
11	acetone	2,3-dimethylbutane	chloroform	760 mmHg	19	0.008	0.008	0.003
12	acetone	2,3-dimethylbutane	methanol	760 mmHg	27	0.007	0.009	0.006
13	2,3-dimethylbutane	chloroform	methanol	760 mmHg	21	0.010	0.007	0.005
Total					553	6.174	5.266	3.923
av.						0.011	0.010	0.007

Nomenclature

Abréviations

LLE	Liquid – Liquid Equilibrium
NRTL	Non-Random Two Liquid activity coefficient model
stu dev	Standard deviation
UNIQUAC	Universal Quasi-Chemical Activity Coefficient model
VLE	Vapor – Liquid Equilibrium

Symbols

G_{ij}	Adjustable parameters in the NRTL model
G^E	Excess Gibbs energy
g_{ij}	Energy of interaction between the i and j component (J mol^{-1})
N	Number of component in the system
P	Total Pressure
R	Gas Constant
T	Temperature
x_i	Mole fraction of component i
z	Coordination number

Greek Letters

α_{ij}	Non-randomness parameter for binary i-j interactions of the NRTL model
γ	Activity coefficient
γ^∞	Infinite dilution activity coefficient
γ_{av}^∞	Average infinite dilution activity coefficient
τ_{ij}	Inherent binary parameter between the i and j component

Subscripts

E	Excess energy
∞	Infinite dilution

Superscripts

av	Average value
caled	Calculated value
exptl	Experimental value
i	component i
j	component j
ij	interaction between the i and j component

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معادلة NRTL المطورة للتنبؤ بأتزان سائل – سائل

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الخلاصة:

الدراسة الحالية تتعامل مع تمثيل بيانات أتزان سائل – سائل الموجود في الأدبيات للحصول على علاقة جديدة للمتغير اللاعشوائي α مناسب للأستخدام في نموذج معامل الفعالية NRTL.

علاقة جديدة مبسطة تم اقتراحها لتطوير نموذج معامل الفعالية NRTL الأصلي ذات الثلاثة متغيرات لجعله نموذج ذات متغيرين. الأداء للعلاقة المقترحة تمت مقارنتها مع نموذج معامل الفعالية NRTL الأصلي ذات الثلاثة متغيرات من خلال تمثيل بيانات أتزان سائل – سائل للأنظمة الثنائية وكذلك للتنبؤ بالأنظمة الثنائية من خلال معامل الفعالية عند التخفيف اللأنهائي والتنبؤ بالأنظمة الثلاثية من البيانات للأنظمة الثنائية.

$$\alpha ij = 0.47\left(1 + \frac{Gij\,Gji}{2.13}\right)^{-1}$$

لضمان ان النتائج صحيحة وذات معنى فيزياوي، المتغيرات التي تم الحصول عليها استخدمت للتنبؤ بمعامل الفعالية عند التخفيف اللانهائي. ان الخواص عند التخفيف اللانهائي مهمة جداً حيث انها تشير الى الدرجة العالية من اللامثالية للأنظمة.

الموديل الرياضي تم تطبيقه بنجاح لحساب أتزان سائل – سائل وكذلك معامل الفعالية عند درجة الحرارة الواطئة. تم جمع قاعدة بيانات واسعة للتحقق من صحة العلاقة والتي تغطي مدى كبير من التركيز ودرجة الحرارة و الضغط. وجد بأن النموذج المقترح للمتغير اللاعشوائي يعطي احسن النتائج.